

## PATEN ABSTRACTS OF JAPAN

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### DETAILED DESCRIPTION

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#### [Detailed Description of the Invention]

art of a hydrocarbon hydrocarbons, especially the aliphatic hydrocarbon which branched for this invention to isomerize a hydrocarbon frame -- when specified further, it is related with the art of olefin hydrocarbon.

Olefin hydrocarbon is used for many various products, for example, alcohol, the ester originating in this and the ether, and an aldehyde list as a start ingredient for final manufacture of an acid etc. in a hydroformylation or an oxo process. In many of these end use, a straight chain or the hydrocarbon (lightly branched) chain which branched for a while has an advantage rather than the chain (heavily branched) which branched.

Furthermore, about oxo process itself, when reactivity says the olefin which has the chain which branched about the specific degree of branching (degree of branching) low rather than what has a straight chain or the structure which branched for a while, a certain kind of isomers have reactivity lower than other things.

If specified further, the thing of the range of C6-C15 will be generated olefin feed especially C4-C20, and often by oligomerization of the original starting material of low molecular weight, and for the rearrangement produced in the reaction time, an approach may produce the olefins in which the high ratio to the extent that it is not a request carried out a large number branching, even if this Hara matter is a straight chain. Furthermore, the locations of the branching are the location which approached mutually on the hydrocarbon chain, the center sections of the chain, or those both, and this originates in oligomerization falling the reactivity of this molecule further

in an oxo reaction.

There is also another field the fewer hydrocarbon which branched is [ field ] convenient, and there is alkylation by the reaction with the olefin of aromatic hydrocarbon concerning [; that it can come and ] manufacture of a surfactant and a polyolefine stabilizer.

Therefore, there is the need of offering the approach of falling the degree of branching of the hydrocarbon matter.

The olefin hydrocarbon matter which branched can be understood by that the degree of branching of this matter falls now by contacting the catalyst which is the configuration of the molecule sieve which it has in 10 membered-ring (10-membered ring) pore structure.

Since the isomer which branched is thermodynamically more stable than the isomer fewer than this which branched, this opinion deserves surprise. the [ furthermore, / that this opinion can isomerize a straight chain olefin to the olefin which branched by contacting ZSM-23 which are the zeolite which has the above-mentioned structure for this, for example, the example which brings about isomerization to the isobutene of n-butene, / Europe patent ] -- EP-B -247802

Surprise is deserved when the content of the number is taken into consideration.

U.S. Pat. No. 5157194 is 10 [ another ]. - When microcrystal ZSM-22 which are a membered-ring zeolite are used, the same result [ say / reporting that the yield from supplied n-butene to isobutene is high ] has been obtained.

the [ International Patent Publication ] -- WO 91/18851 In the number, since the part of Lewis acid is produced, the approach of interconversion that the unsaturated compound using the catalyst containing the molecule sieve by which the ion exchange was carried out with the cation, for example, a carbon atom, includes isomerization of 3-9 n-olefins is indicated. The suitable molecule sieves are a silica / alumina phosphate (SAPO), and zeolites. In case n-butene isomerizes conditions desirable to isomerization easily to isobutene, the range of 250-500 degrees C especially of temperature is 375-475 degrees C, and a pressure is atmospheric pressure especially mostly 0.08 to 0.12 MPa.

the [ Europe patent disclosure ] -- EP-A -523838 while the number is indicating the approach of resemblance isomerization to the alkenes which straight chain alkenes branched -- the [ International Patent Publication ] -- WO 93/03118 The number is indicating the approach of contacting two sorts of catalysts continuously, in order to raise the content of the alkene which

branched the supplied alkene.

This invention is the approach of falling the degree of branching of the olefin feed which branched, and is this raw material 10 - The approach of including contacting under conditions which promote isomerization of a frame in the molecule sieve which has membered-ring pore structure is offered.

although this invention is applicable to all the olefin kinds that branched -- especially -- a carbon atom -- 4-20 olefins -- if specified further -- a carbon atom -- 7-16 olefins -- and a carbon atom can especially apply to 7-12 alkenes. The feed for this reaction can be the mixture of two or more sorts with equal single kind and carbon atomic number of alkene isomers or the mixture of two or more sorts of alkenes which have width of face in a carbon atom, for example, the mixture of C7-C12.

This invention is especially applicable to the mixture of an olefin kind with which the degree of branching exceeds 1.80 and which exceeds especially 1.95 to the nonene mixture which has the above-mentioned degree of branching, if specified further. The degree of branching (D) of olefin mixture which has various numbers of branching is defined by the following type. :

$D = (my + nz + \text{etc}) / (x + y + z + \text{etc})$  (mole-ratio; z of the kind with which mole-ratio; y of the kind which X does not branch among a formula has branching of m individual is n. it is the mole ratio of a seed which has branching of an individual (etc)).

10- 10 with an aluminosilicate, alumino phosphate (AlIPO), SHIRIKO alumino phosphate (SAPO), METARO alumino phosphate (MeAPO), and METARO alumino phosphoric-acid silicate (MeAPOS) typical as an example of a molecule sieve which has membered-ring pore - A membered-ring can be mentioned. However, it is 10 when it states to a detail further. - It is ISI-1 to membered-ring zeolites, ZSM-5 [ for example, ], ZSM-22, ZSM-23, ZSM-48, and a list. And KZ-2 can be mentioned. Or it dehydrated, these zeolites are usually used with an acid ( $H^+$ ) mold, where hydration is carried out selectively. the baking conditions of a zeolite at the time of extent of hydration removing this, when organic mold (organic template) (structure which shows a reagent) is used in manufacture of this zeolite -- or it is adjusted by the hydration of this feed. the above-mentioned zeolite needs to be calcinated because of the existence of mold -- if it becomes -- inactive -- or it has oxidized -- it can carry out before an activity in the range whose temperature is usually 350-550 degrees C in one of those atmospheric air.

This crystal can be the extrusion object manufactured with powder, granulation, or other molding articles, for example, mixture with a suitable binder. this catalyst has good temperature of 350-700 degrees C and convenience -- corks combustion (coke burn) in 400-550-degree C air -- or to it being convenient, it is easily reproducible with 350-550-degree C steam treatment.

Extensive conditions can apply to isomerization. 50-350 degrees C of isomerization can be preferably carried out to it being convenient at the temperature of the range of 150-250 degrees C. The convenient pressure for this reaction is the range of atmospheric pressure to 7.5MPa(s) preferably 10 MPas from atmospheric pressure. This reaction can be performed with this feed, a reaction mixture, and a product in a gas, a liquid, a gas/liquid, or a dense phase (dense phase) according to the temperature and the pressure which were used. This feed can consist of an olefin reactant substantially, or can contain an olefin in inactive diluents, such as an alkane, or mixture with a solvent as support.

This reaction can be performed with a batch method like an autoclave, or a continuous magnetization method. In a continuous magnetization method, WHSV of activity feed has the preferably convenient range of 1-2W/Wh Wh 0.25-5W /.

In addition to falling the average degree of branching of the supplied mixed olefin, the approach of this invention changes the location of 1 or two or more ramification in this olefin feed further. The effect of this modification produces a product which the number of the carbon atoms between branching is increased, and that branching generally separates from the center of this molecule more, and is more far apart. Although it naturally is not possible to identify a reaction separately in the olefin feed with which the number and location of branching are intermingled, a synthetic observation result is as above-mentioned.

For example, the result in the case of using the supplied mixed nonene can collect that the rate of 3 and 4-dimethyl heptene decreased, while 2 and 5-dimethyl heptene increases in addition to reduction of the rate of dimethyl hapten, and the increment in the rate of methyl octene.

This isomerization is independent, or is coincidence or sequential either, and can be used combining other reactions.

Therefore, this invention is 10 under conditions which convert to the olefin which branched an olefin or non-olefin starting material, and promote isomerization for the obtained olefin. - The approach of contacting to the molecule sieve which has membered-ring pore structure, and

converting this isomerized olefin product into a request, a different olefin, or a non-olefin kind, if required is also offered.

Furthermore, this invention is 10 under conditions which promote isomerization for the olefin which branched. - The molecule sieve which has membered-ring pore structure is made to contact, the olefin product by which the parenthesis was isomerized is converted into a different olefin or a different non-olefin kind, and if required, the approach of forming the olefin which branched from the different non-olefin or the different olefin kind from a request or the isomerized thing will also be offered.

As an example of the approach of as [ a start ingredient or an end product is not an olefin ], the this isomerized olefin product can mention the above-mentioned method of receiving a hydroformylation.

The above-mentioned start ingredient as an example of the reaction sequence of as [ whose isomerized thing of the is a different olefin kind ] A low-molecular-weight olefin, for example, a propene, or a butene is oligomerized. It becomes the isomerized above amount olefins of macromolecules at the olefin of higher molecular weight, for example, octene, nonene or a dodecane, and a list. After that this isomerized olefin That which is used for arbitration as feed of a hydroformylation, or is oligomerized further can be mentioned.

The degree of branching produces high oligomer mixture, such \*\*\*\*\* uses the oligomerization catalyst based on a solid phosphoric acid, H-ZSM -5, an acid silica, an alumina, a mixed silica / alumina, or a transition-metals metal as a catalyst, and oligomerizes an olefin with little supplied branching (light olefin), it is the approach of this invention after that, and the frame of this mixture is isomerized, and if it is a request, it can classify this oligomer mixture beforehand. This product is oligomerized further or is used as feed of a hydroformylation.

Although it can carry out in a different reactor, this of isomerization following this oligomerization and it is desirable when necessarily not needing to be isomerized. a case so that the oligomer mixture with which this was indicated in this application description, or a downstream product may occasionally be produced at a certain time and the first oligomerization may not sometimes arise -- it is --; -- this oligomer can be analyzed and required -- if it becomes, this isomerization machine will be arranged at flow.

Since the reaction condition of oligomerization and isomerization is substantially the same, when

by contrast isomerization is always required, the catalyst of this oligomerization and isomerization can be mixed and arranged [ be / it / under / same reactor / continuation ]. The mixture of the same catalyst of a floor is two sorts of zeolite catalysts, ZSM-5 [ for example, ]. And the mixture of ZSM-22 is convenient.

It is the unreacted olefin which was preferably separated from the resultant removed from this reactor instead in addition to isomerization of the oligomer olefin supplied to the reactor, for example, the reactor for hydroformylations, and was reused to this reactor, and isomerization may be performed. As mentioned above, the olefins which branched have reactivity lower than the isomers which branched few in an oxo process.

In the activity according to which usual [ of an oxo process ] was industrialized, since it is not converted to the product by which all the olefins in this feed were oxygenated, it dissociates from this oxygenated quality of a product, and unreacted starting material is reused. By this reaction approach, in the reused matter, since a kind with low reactivity is manufactured, this brings about serious loss of effectiveness substantially.

About said unreacted olefins, before these reuse by using the isomerization process of the frame of this invention, it is converted more to a reactant high kind. Therefore, especially this invention separates an unreacted olefin from a resultant after a hydroformylation, and is 10 under isomerization conditions. - The approach of the hydroformylation of olefin feed which is contacted to the molecule sieve which has membered-ring pore structure, and is returned to this hydroformylation reaction is offered.

The hydroformylation which should be performed with a low invert ratio is possible for this approach, and it decreases by this in a by-product (heavy species), for example, the kind which branched, and paraffin, and has the advantage of promoting the consumption cutback of oxo-catalysts. Furthermore, when, as for the average reactivity of the olefin supplied to this reactor, only an unreacted olefin is exposed to isomerization, this increases from the reason for probably having the high degree of branching more efficiently rather than what was supplied first.

:example 1 which explains this invention to a detail in the following example In this example, supply of diluent branch nonene is used as feed in a continuous process.

The conditions acquired in a dense phase are as follows.

Feed 3 % of the weight of nonene fractions in a propane Catalyst H-ZSM -22 Tooth-space rate

1.6 g/gh. (based on a nonene content.)

Temperature 200 degrees C Pressure 7 MPa Reactor A continuous flow, the fixed bed Time amount 5 hours Feed which reacts C8- 0.8% Constituent (weight ratio) C9+C10 97.6% C11+ 1.6% The following table 1 shows the presentation about branching in the nonene fraction and feed which were collected over each time amount, and a product. After carrying out the hydrogen treating of all the analysis on a line, it was carried out with the gas chromatography.

表 1

アイソマー		直 鎖	1 - Br	2 - Br	3 - Br	D
	供給	1.22	8.81	75.96	14.01	2.03
生成	0.6 to 1.1h	0.00	26.54	62.60	10.86	1.84
	2.2 to 2.6h	1.30	26.57	59.35	12.79	1.84
	4.3 to 4.7h	0.68	27.23	60.88	11.21	1.83

省略記号：

h = 時間      1 - Br = 単一の分枝

D = 分枝度

The following table 2 shows each isomer mol fraction of the nonene in the feed and the product covering each time amount.

A table 3 shows the rate (% of the weight) of the compound of various carbon atomic numbers in the feed and the product covering each time amount. The gas chromatography performed measurement.

From the result of said tables 1-3, reduction of the degree of branching of nonene which begins from reduction of two branching accompanying the increment in reduction [ of 3 and 4-dimethyl heptene ] and 2, and 5- and 2, and 6-isomer and the increment in single branching is shown.

Example 2 In this example, the nonene which does not dilute was used at the batch process

process. The reaction condition was as follows.

Feed : 100% Nonene fraction (the same presentation as an example 1)

Catalyst liquid reactor: H-ZSM 22, 10% of the weight of feed Temperature : 200 degrees C

Pressure : 300 KPa Phase : : Stirring type autoclave time amount : The 9.5 hour table 4 shows the presentation about branching of the nonene fraction sampled to declared time amount, feed, and a reaction mixture.

A table 5 shows the mol fraction of the isomer of 2 branching nonene after predetermined time progress.

Distribution of a product resembles dramatically distribution of the example 1 shown in tables 1 and 2 as the result of tables 4 and 5 shows, and shown by the nonene isomer 9.5 hours after.

Example 3 The reaction was performed within the autoclave made into the self-heating pressure. Temperature was maintained at 165 degrees C for 24 hours. Feed is 50g of isomer mixture of a heptene, and the catalyst used 10g of H-ZSM-22 powder.

A table 6 shows the presentation of feed and an end product.

Example 4 This example is the autoclave which carried out the self-heating pressure, and was performed like the example 3. Feed is the mixture of octene and a nonene isomer and octene forms main fractions.

Temperature was maintained at 190 degrees C for 24 hours, using 10% of the weight of H-ZSM-22 catalyst of feed.

The result was shown in tables 7 and 8.

Example 5 The example 4 was repeated except for having made the catalyst into 20 % of the weight. The result was shown in tables 9 and 10.

Example 6 Although the example 4 was repeated, the octene mixture obtained according to dimerization of an isobutylene was used as feed. Temperature was held at 200 degrees C. A result is shown in a table 11 and a table 12.



Example 7 Nonene feed was used although the example 4 was repeated. A result is shown in a table 13.

Example 8 In this example, the catalyst was H-ZSM -22 of the 3mm extrusion mold used with 10% of the weight of a nonene feed stock. Isomerization is 200 degrees C in natural pressing down and an autoclave, and was performed for 24 hours. A result is shown in a table 14.

Example 9 Although the example 8 was repeated, isomer-ization was performed in 6 hours. A result is shown in a table 15.

The comparison of examples 8 and 9 shows that making an isomer-ized reaction extend makes the degree of ramification lower. However, this is based on contention of the oligomerization at the sacrifice of reducing yield.